ISSN 2706-655X Vol.4, Issue 6: 50-55, DOI: 10.25236/IJFET.2022.040608

Preparation and Properties of a Kind of Tellurium Bismuthate Mid-infrared Luminescent Composite Glass

Dan Wang[a,*], Jinying Huang[b]

School of Optoelectronic Science, Chanchun College of Electronic Technology, Changchun, 130114, China
[a]261468810@qq.com, [b]berry924@sina.com
**Corresponding author*

Abstract: *The band of infrared luminescence includes atmospheric windows of 1-3μm, 3-5μm, and 8-14μm, covering many important characteristic spectra. Therefore, the luminescent materials in this band are used in biomedical, satellite remote sensing, weapon guidance, industrial processing, Weapon penetration and other fields have broad application prospects. In this paper, the preparation method of doped bismuth telluride composite glass material was studied, and the luminescence properties of infrared luminescent composite glass in the 2.7μm band mid-infrared laser in the matrix material. In this paper, the TeO_2-Nb_2O_5-Bi_2O_3 glass system was selected as the matrix glass to prepare the tellurate infrared emitting composite glass. The Bi3.20Te0.80O6.40 crystal is a three-dimensional growth method, and the nucleation and growth process of the glass-ceramic is a diffusion mechanism, which belongs to the crystallization behavior mainly controlled by diffusion. Transparent bismuth telluride composite glasses with different doping concentrations of rare earth ions were prepared by a two-step heat treatment method. The infrared luminescent composite glass prepared in this paper has strong penetrating ability to smoke and atmosphere, good transmission confidentiality and low loss, and has important application prospects in radar systems, infrared remote sensing, laser ranging and other fields. The final results of the study show that, by comparing the melting and purity of chemical reagents, it can be seen that the melting time consumed by bismuth oxide is 45 minutes, and a purity of 95.5% can be obtained. The time is shorter, which is conducive to reducing a certain cost.*

Keywords: *Bismuth Telluride, Composite Glass, Infrared Emission, Diffusion Mechanism*

1. Introduction

The luminescent glass doped with bismuth telluride bismuth oxide has attracted more and more attention in the application of light-emitting devices, and has received a lot of attention because of its application in lighting devices and operating room lighting equipment. Tellurium bismuthate has a unique ionic structure, which can improve the transparency and stability of glass [1]. Thus, the luminous intensity of the luminescent glass of tellurium bismuthate is increased. Moreover, it emits fluorescence under a certain wavelength of light excitation, and has excellent color purity and stable luminescence performance. Therefore, this paper has certain experimental significance for the preparation and performance of a tellurium bismuthate mid-infrared luminescent composite glass.

In recent years, many researchers have studied the preparation and properties of a kind of tellurium bismuthate mid-infrared luminescent composite glass, and achieved good results. For example, Berwal N believes that the use of infrared light-emitting composite glass can well distinguish the distribution of light sources without the effect of infrared and ultraviolet rays, and achieve better results [2]. Grabov VM believes that the generation technology of near-mid-infrared light mainly uses rare-earth ion-doped luminescence, semiconductor luminescence and nonlinear luminescence, among which amplifiers developed with rare-earth doped elements have brought revolutionary changes to the field of near-mid-infrared lightwave technology [3]. At present, domestic and foreign scholars have carried out a lot of research on the preparation and properties of infrared emitting composite glass. These previous theoretical and experimental results provide a theoretical basis for the research in this paper.

In this paper, based on the theoretical basis of the preparation technology of tellurium bismuthate, combined with the preparation and performance of mid-infrared luminescent composite glass, the

ISSN 2706-655X Vol.4, Issue 6: 50-55, DOI: 10.25236/IJFET.2022.040608

formation zone of the glass system was predicted by thermodynamic method, and the point-by-point method was used to verify it. Then, we investigated the crystallization kinetics of the bismuth telluride glass system. Then, a luminescent composite glass containing Bi3.20Te0.80O6.40 nanocrystals with controllable crystallization was obtained by a two-step heat treatment method, and a strong mid-infrared fluorescence emission was obtained in the luminescent composite glass.

2. Related Theoretical Overview and Research

2.1 Properties and Preparation Methods of Tellurium Bismuthate

Bismuth telluride glass is a new type of heavy metal oxide optical glass that has appeared in recent years. Bi belongs to the main V group of the sixth period of the periodic table, the ion beam is large, and the electronegativity is weak, so Bi-O is weak and cannot form glass by itself. The introduction of network-forming bodies such as B2O3 and Si_2O_3 can significantly improve the physical and chemical properties of glass [4-5]. With the decrease of Bi/Si ratio, the Si-O-Si bond angle increases, the Si-O bond ionicity increases, and the glass transition temperature increases significantly. Optical bandwidth, electron polarization capacity, and photobasicity are all closely related to the Bi/Si ratio.

An important feature of bismuth telluride glass is its high refractive index and high nonlinear third-order refractive index, which shows broad application prospects in all optical switches, full-wave converters, and supercontinuum spectroscopy. Bismuth telluride-impregnated II-VI microcrystalline materials have potential applications in imaging, biomedicine, and laser fields due to their high quantum luminescence efficiency, high optical gain, and low confinement [6]. Producing high-quality optical micro-nano materials is an effective way to optimize high-efficiency bismuth telluride:II-VI mid-infrared composite lasers and green hot-pressed ceramic green materials. There are three commonly used preparation methods:

(1) The pellet milling method first uses conventional methods, such as high temperature diffusion, to obtain bismuth tellurium crystals: II-VI, then pulverize the crystals and mix them with a certain proportion of balls, and put them into a mill for ball milling. Usually, TM^{2+}: II Available at the micron scale. However, conventional crystal preparation methods, such as high-temperature diffusion, take a long time, the obtained crystals have uneven doping concentration, and the nanocrystals obtained by ball milling are small in size and take a long time to obtain. The particle size distribution is not uniform.

(2) The laser sputtering method utilizes high-energy pulsed laser to disperse polycrystalline bismuth telluride: Objective II-VI to prepare nano-scale (3~250nm) tellurium II-β under the protection of inert atmosphere. However, this method has high energy consumption, low efficiency, high-energy nanocrystals are easy to agglomerate after spraying, and the powder dispersibility is poor.

(3) The chemical synthesis method matches the doping concentration through the stoichiometric reaction, and uses the intra-ionic compound reaction under certain conditions (temperature, pressure, etc.) to obtain nano-scale bismuth tellurium: particles II-VI, the particle size is OK, but at present, the main use for tuning the production of fluorescent nanocrystals in the UV and visible regions.

In recent years, researchers have attempted to create chemically synthesized mid-infrared photometric nanocrystals. Co^{2+}:ZnSe nanocrystals with mid-infrared emission properties of ~3.5μm at 293K were obtained by a one-step method using thioglycolic acid as a stabilizer. In addition, Fe^{2+}:ZnSe quantum dots were prepared using the hydrothermal microemulsion composition, and the mid-infrared emission in the 3.5-4.5μm band was obtained at low temperature of 35-200 K. environment and low cost [7-8]. In particular, the hydrothermal method is the best choice among chemical methods, because it can produce nanoscale particles with narrow particle size distribution and low accumulation, and has the advantages of low cost, simple operation, environmental friendliness, low toxicity, and simple process. Less impurities and high stability.

However, for most of the previous studies, chemically prepared TM^{2+}:II-VI transition metal ion semiconductor nanocrystals showed severe fluorescence damping in the mid-infrared due to the organic phase and the high density of surface defects introduced during the process. Spectral regions have poor visual properties. Therefore, reducing the use of organic ligands and improving the surface lattice environment of nanocrystals are effective means to improve the emission performance of dielectric pro, chemically prepared semiconductor nanocrystals TM^{2+}:II-VI.

ISSN 2706-655X Vol.4, Issue 6: 50-55, DOI: 10.25236/IJFET.2022.040608

2.2 Introduction to Mie Scattering Theory

One of the main requirements of composite infrared glasses for optical materials is a low level of light scattering losses. This can be achieved when the average size of the introduced particles is much smaller than the wavelength of the emitted radiation. Therefore, the Mie scattering theory was introduced, which was used to perform preliminary calculations to estimate the size and concentration values of particles (or volume fractions) limited by the desired level of light loss [9]. Mie scattering, also known as "coarse particle scattering", is the phenomenon of particle scattering where the particle size is close to or larger than the wavelength of the incident light. This relationship first came from the German scientist M. It has the following characteristics:

(1) The scattering intensity is much higher than that of Rayleigh scattering, and the variation of scattering intensity with wavelength is not as strong as that of Rayleigh scattering. As the scale parameter increases, the total scattered energy increases rapidly and finally tends to a certain value in the form of vibrations. Rare earth luminescent materials have the advantages of strong absorption capacity, high color purity and high conversion efficiency, especially in the visible light region.

(2) The intensity of scattered light has many maxima and minima as the angle changes. When the scale parameter increases, the number of extrema also increases. Moreover, the rare earth doped luminescent glass ceramics has the advantages of high light transmittance, isotropy of glass, thermal stability of ceramics, good mechanical strength, etc. Compared with phosphor materials, it has better color rendering index and longer service life.

(3) When the scale parameter increases, the ratio of forward scattering to backward scattering increases, thereby increasing the scattering of particles in the front hemisphere. When the scale parameter is small, the Mie scattering effect can be reduced to Rayleigh scattering [10]. Nanocrystalline particles with high chemical activity have poor monodispersity and are difficult to distribute uniformly in the doped matrix, which increases the difficulty of drawing optical fibers. Therefore, specific treatment of nanocrystal surfaces is required to improve the agglomeration effect of nanocrystals. Commonly used methods mainly include lyophilization, core-shell coating46 and the use of surfactants to prevent caking [11-12]. Among them, there are many hydroxyl residues in the freeze-drying process, and the surfactant is an organic solvent, which has strong absorption in the mid-infrared band.

3. Experiment and Research

3.1 Experimental Method

The density of the glass samples was measured by the Archimedes drainage method, using distilled water as the immersion liquid. Calculate the density of the glass sample according to the formula:

$$d = \frac{m_1}{m_1 - m_2}\left(p - 0.0012\right) + 0.0012 \tag{1}$$

$$N_0 = \frac{d}{M} \times mol\% \times N_A \tag{2}$$

In the formula, m_1 is the weight of the glass sample in air, m_2 is the weight of the glass sample in distilled water, P is the density of distilled water at room temperature, and 0.0012g/cm^3 is the density of air at room temperature.

3.2 Experimental Requirements

Based on the XGBoost algorithm, this experiment carried out research on the prediction of English online network performance. Through glass synthesis chemical reagents and melting analysis and differential thermal (DSC) curve analysis of precursor glass samples, the experiment passed the requirements of infrared luminescent composite glass. The chemical reagent and the experimental melting time were compared and analyzed, and the feasibility of the reagent was judged according to the obtained purity, and the influence of the content of bismuth oxide and the experimental temperature on the preparation purity at different temperatures was analyzed, and the collected data were analyzed.

4. Analysis and Discussion

4.1 Glass Synthesis Chemical Reagents and Melting Analysis

In the experiment, the chemical reagents required for the infrared luminescent composite glass and the experimental melting time were compared and analyzed, and the feasibility of the reagents was judged according to the obtained purity. The experimental data is shown below.

Table 1: Glass synthesis chemical reagents and melting analysis table

Chemical Reagent	Fusion(min)	Purity(%)
Bi_2O_3	45	95.5
GeO_2	58	80.6
SiO_2	72	91.6
Na_2CO_3	90	88.9

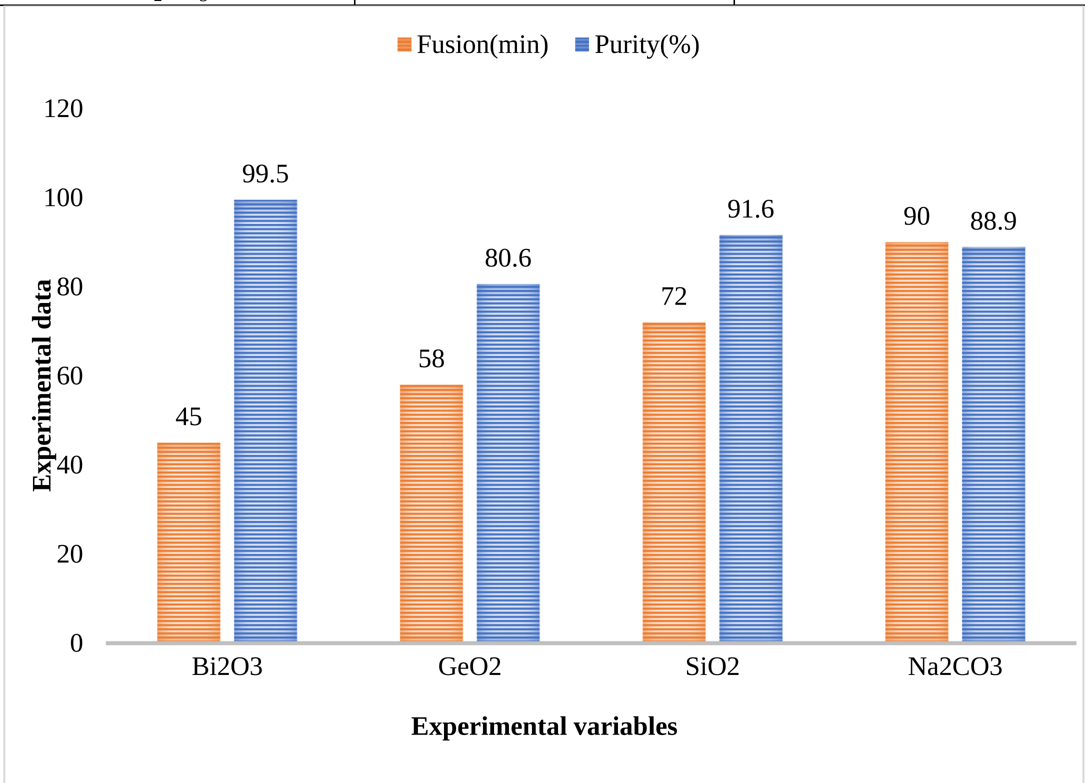

Figure 1: Glass synthesis chemical reagents and melting analysis diagram

As can be seen from Figure 1, it can be seen by comparing the melting and purity of chemical reagents that the consumed melting time of bismuth oxide is 45 minutes, and the purity of 95.5% can be obtained, and the consumed melting time of germanium oxide is 58 minutes, the purity of 80.6% can be obtained, the consumed melting time of silicon dioxide is 72 minutes, and the purity of 91.6% can be obtained, and the consumed melting time of sodium carbonate is 90 minutes, and the purity of 89.9% can be obtained, It can be seen from this that the raw material prepared by bismuth oxide has better purity and consumes less time, which is beneficial to reduce certain costs.

4.2 Differential Thermal (Dsc) Curve Analysis of Precursor Glass Samples

Through glass synthesis chemical reagents and melting analysis, the raw materials prepared by bismuth oxide have better purity and less time consumption. The experiment continues to analyze the differential thermal (DSC) curve of the precursor glass sample. The experimental data is shown in the Figure 2.

As shown in Figure 2, when the differential heat of different glass samples was tested respectively, at 300℃, the bismuth oxide was 25mol%, the purity was 80.5%, and at 400℃, the bismuth oxide was 35mol%, the purity was 82.7%, At 500℃, the bismuth oxide is 45mol% and the purity is 88.4%. At

300℃, the bismuth oxide is 65mol% and the purity is 99.5%. At 700℃, the bismuth oxide is 75mol% and the purity is 92.6%. The purity of the luminescent composite glass prepared when the bismuth oxide content is 65mol% is the highest at 600℃.

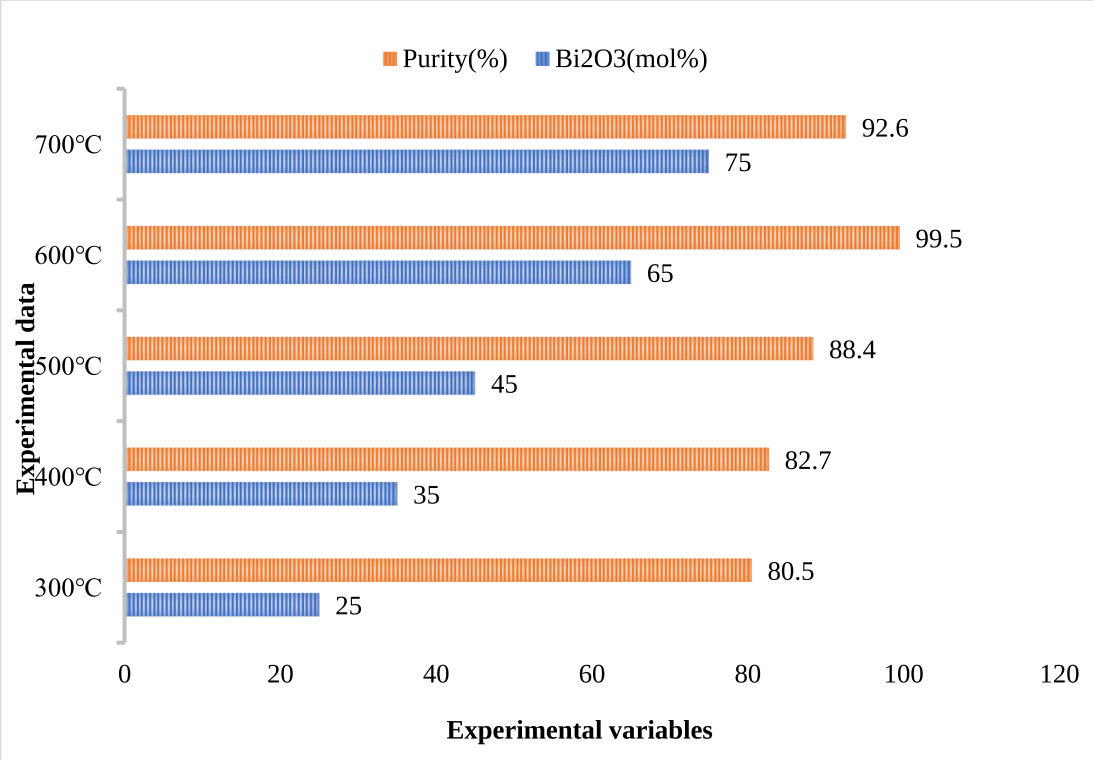

Figure 2: Comparative analysis of algorithm clustering accuracy

5. Conclusions

In this paper, based on the preparation technology of tellurium bismuthate, the preparation and properties of infrared emitting composite glass are studied, and a series of experiments are carried out to prove that the preparation technology of tellurium bismuthate has certain feasibility in infrared emitting composite glass. It can be seen from the experimental data of the differential thermal (DSC) curve analysis of the synthetic chemical reagent and the precursor glass sample, by comparing the melting and purity of the chemical reagent, it can be seen that the raw material prepared by bismuth oxide has better purity and consumes more time. It is beneficial to reduce a certain cost, and the purity of the luminescent composite glass prepared when the temperature is 600℃ and the bismuth oxide content of 65 mol% is the highest. The tellurium bismuthate glass has good stability and strong adaptability, and can play a good role in different refractive indices and densities. The tellurium bismuthate used to prepare infrared emitting composite glass can maximize its performance. The tellurium bismuthate glass has a good application prospect in the infrared emitting composite glass and various lighting fields.

References

[1] Girsova M A, Golovina G F, Kurilenko L N, et al. Spectral-Luminescent Properties of Composite Materials Based on Nanoporous High-Silica Glasses Activated with Bismuth and Cerium Ions. Glass Physics and Chemistry, 2021, 47(4):353-359.

[2] Berwal N, Ahlawat N, Mohan D, et al. Study of Vibrational Spectroscopy, Linear and Nonlinear Optical Properties of Borate-Modified Tellurium–Silica–Bismuthate Glasses. 2020, 10(5):8-15.

[3] Grabov V M, Demidov E V, Komarov V A, et al. Galvanomagnetic Properties of Bismuth–Antimony Films under Conditions of Plane Tensile Strain. Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques, 2021, 15(4):777-780.

[4] Mohammadi M, Mehdipour-Ataei S. Preparation and Properties of Composite Membranes of Fully Fluorinated Nanofibrous Electrospun Mat Impregnated with Highly Sulfonated Polysulfone: Effect of

ISSN 2706-655X Vol.4, Issue 6: 50-55, DOI: 10.25236/IJFET.2022.040608

Thermal Treatment on the Mat and the Membranes Thereof. International Journal of Hydrogen Energy, 2022(1):8, 17(5):10-15.
[5] Alekseev R O, Savinkov V I, Sigaev V N. Investigation of the Structure and Properties of Glasses in the System La_2O_3*–MnOm–*B_2O_3*(M = Nb, Ta, Ti, Zr). Glass and Ceramics, 2022, 78(11-12):467-470.*
[6] A S V, A J W J, A N N T P, et al. Near-Infrared Absorption and Photothermal Properties of Heptamethine Pyrylium Dyes With Bistriflimide Anion. Dyes and Pigments, 2022(3):1-20。
[7] Barbooti M M, Al-Dabbagh B D, Hilal R H. Preparation, Characterization and Utilization of Polyacrylic Acid–Kaolin Composite in the Removal of Heavy Metals From Water. 2019, 39(4):350-371.
[8] Bauer A, RNer K, Lehnhardt T, et al. Mid-Infrared Semiconductor Heterostructure Lasers for Gas Sensing Applications. Semiconductor Science and Technology, 2019, 3(19):46-55.
[9] Colley C S, Hebden J C, Delpy D T, et al. Mid-Infrared Optical Coherence Tomography. Review of Scientific Instruments, 2020, 78(12):1178-1189.
[10] Marchi M D, Toffanin V, Cassandro M, et al. Invited review: Mid-Infrared Spectroscopy as Phenotyping Tool for Milk Traits1. Journal of Dairy Science, 2014, 97(3):1171-1186.
[11] Chary R R. Insights into Galaxy Evolution from Mid-infrared Wavelengths. 2019, 47(9):772-795.
[12] Hati K M, Sinha N K, Mohanty M, et al. Mid-Infrared Reflectance Spectroscopy for Estimation of Soil Properties of Alfisols from Eastern India. 2022, 2(12):84-89.